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Rapid removal of atmospheric CO₂ by urban soils

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1 TOC/Abstract art



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4 **Abstract**

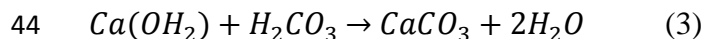
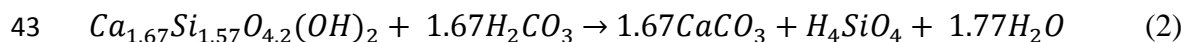
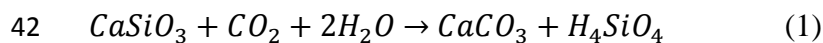
5 The measured calcium carbonate content of soils to 100 mm depth at a large urban
6 development site has increased over 18 months at a rate that corresponds to the
7 sequestration of 85 tonnes CO₂ per hectare (ha⁻¹) (8.5 kg CO₂ m⁻²) annually. This is a
8 consequence of rapid weathering of calcium silicate and hydroxide minerals derived from
9 demolition of concrete structures, which releases Ca that combines with CO₂ ultimately
10 derived from the atmosphere, precipitating as calcite. Stable isotope data confirm an
11 atmospheric origin for carbonate-carbon, and ¹⁴C dating indicates the predominance of
12 modern carbon in the pedogenic calcite. Trial pits show that carbonation extends to depths
13 of 1 m or more. Work at other sites shows that the occurrence of pedogenic carbonates is
14 widespread in artificially created urban soils containing Ca and Mg silicate minerals.
15 Appropriate management of less than 12,000 hectares of urban land to maximise calcite
16 precipitation has the potential to remove 1 million tonnes of CO₂ from the atmosphere
17 annually. The maximum global potential is estimated to be approximately 700-1,200 Mt
18 CO₂ per year (representing 2.0-3.7% of total emissions from fossil fuel combustion) based
19 on current rates of production of industry-derived Ca and Mg-bearing materials.

Introduction

There is a global commitment to reduce greenhouse gas emissions; the UK Government is currently committed to an 80% reduction by 2050 (against a 1990 baseline). A number of approaches envisage ways in which climate mitigation could be achieved practically.

Pacala and Socolow (2004) estimated that 26 Gt CO₂ a⁻¹ by 2050 of CO₂ would need to be removed from the atmosphere in order to compensate wholly for anthropogenic emissions. They propose that a number of individual mitigation approaches may potentially be used in unison to remove equally sized ‘stabilisation wedges’ of 4 Gt CO₂ a⁻¹ each by 2050. This view is revised by Davis et al (2013), who recognise that continued growth in annual emissions since 2003 required more wedges than previously considered, and stress the importance of supporting energy technology innovation to achieve the required targets.^{1,2}

Soils emit almost 275 Gt CO₂ a⁻¹ as a consequence of plant root respiration and the mineralisation of organic carbon, and so they have an important influence on climate. The inorganic carbon content in soils is dominated by calcium and magnesium carbonate minerals.³ During weathering, Ca and Mg silicate and carbonate minerals naturally react with dissolved carbon dioxide (CO₂) to increase local alkalinity. Given the right conditions, some of this dissolved CO₂ precipitates as secondary carbonate minerals in the soil. If the Ca or Mg in the carbonate is derived from silicate weathering, and weathering products, this process provides a means of effectively capturing and fixing atmospheric CO₂.^{4,5,6} Examples of carbonation reactions are given below, using for illustrative purposes wollastonite, a natural calcium silicate (reaction 1), jennite, a hydrated cement mineral (reaction 2), and portlandite, a component of Portland cement (reaction 3):



45 The precipitation of carbonate minerals as a consequence of silicate weathering contributes
 46 to the stabilisation of atmospheric CO₂ over geological time periods^{4,7} and also contributes
 47 to the formation of pedogenic carbonates in both natural⁸ and artificial soils⁹ over much
 48 shorter timescales. Limited information is available for the formation of pedogenic
 49 carbonates in UK soils, with Rawlins (2011)¹⁰ estimating the total inorganic carbon stock
 50 of soil (0–30 cm depth) to be 186 Mt C, around 5.5% of the estimated total soil carbon
 51 stock (organic and inorganic) across the UK.

52 Work on the in situ weathering of natural and artificial silicates^{9,11-20} has shown that
 53 artificial silicates and mineral wastes (such as construction and demolition waste, iron and
 54 steel slag and mine tailings) in soil settings rapidly weather with the associated formation of
 55 carbonate minerals. This process is influenced by a number of physical and environmental
 56 factors including small particle size and high surface area, poor crystallinity and degree of
 57 exposure through proximity to the ground surface or position relative to the water table. In
 58 this way, artificial silicates have the global potential to capture 700-1200 Mt CO₂ a⁻¹,
 59 representing 2.0-3.7% of contemporary global CO₂ emissions (currently global annual CO₂
 60 emissions account for approximately ~33 Gt CO₂ a⁻¹), or one sixth to one third of a
 61 stabilisation wedge.^{1,21} Natural silicates present a carbon capture potential orders of
 62 magnitude greater.²⁰

Studies in urban soils^{9,16} demonstrate a carbon capture potential of 12.5 kg CO₂ tonne soil⁻¹ a⁻¹ by this process, showing that formation of these pedogenic carbonate minerals in urban soils may be a significant and exploitable storage route for soil carbon. An increasing number of studies^{9,12,14-19} have focussed on the carbonation of artificial and waste minerals in this context, due to their abundance and ability to provide a readily available and accessible analogue for the intentional carbonation of natural minerals.

In the present study we measured soil carbonate formation over 18 months, with accurate resampling of a subset of the original sample points achieved using high resolution GPS. This is the first time that a study of this kind has directly measured changes in soil inorganic carbon content in urban soils over time. We quantifiably show that CO₂ sequestration from the atmosphere can occur rapidly over months to years, even where sites are not intentionally managed for this purpose. Using stable and radiogenic isotope analysis, we unambiguously demonstrate the sequestration of modern atmospheric carbon dioxide. The results of this study suggest that the management of urban soils constitutes a promising and relatively inexpensive process for removing CO₂ from the atmosphere.

Materials and methods

Newcastle Science Central (World Geodetic System coordinates UK; 54.970406 – 1.626477 (WGS84)) is a 10 ha site that is currently being developed by Newcastle University and Newcastle City Council into a multi-use ‘science, business, living and leisure’ complex.²² The pre-existing complex of brewery buildings was demolished in December 2007, at which point the site was completed with a surface layer (0.2 – 6 m thick) of ‘made ground’ composed of material derived from demolition, including fines from the

onsite production of crushed concrete secondary aggregates. This is typical of modern development practice, which frequently involves on-site crushing to recover a secondary aggregate product while retaining crusher ‘fines’ on site as part of the soil. After demolition, the site remained undisturbed, allowing sparse growth of primary colonising plants (e.g. *Buddleia* sp.), until early 2013 when ground stabilisation work was carried out to remove, replace and compact all material to a depth of 20 m.

Soil samples were collected at 72 points on 16th September 2010¹⁷ and again at 23 of these points on 13th March 2012, located to 25 mm accuracy using Leica GPS equipment (Leica GS15 with a CS16 controller with a Smartnet RTK correction; Fig. 1). At each location, the soil consisted of demolition rubble containing fragments of building materials grading into fines resulting from processing during demolition. 0.5-1.0 kg of this material was collected between 0-100mm depth using hand tools and sieved to <2mm onsite (eliminating large fragments of bricks and concrete, and representing a sub-sample of 30% of the total soil mass).¹⁷ In parallel, 7 trial pits, to investigate carbonate formation with depth, were excavated to a depth (where possible) of up to 3 m, on 13th March 2012, taking samples of 0.5-1.0 kg at approximate intervals of 0.5 m. All samples were air dried, crushed and sieved to <63µm prior to analysis.

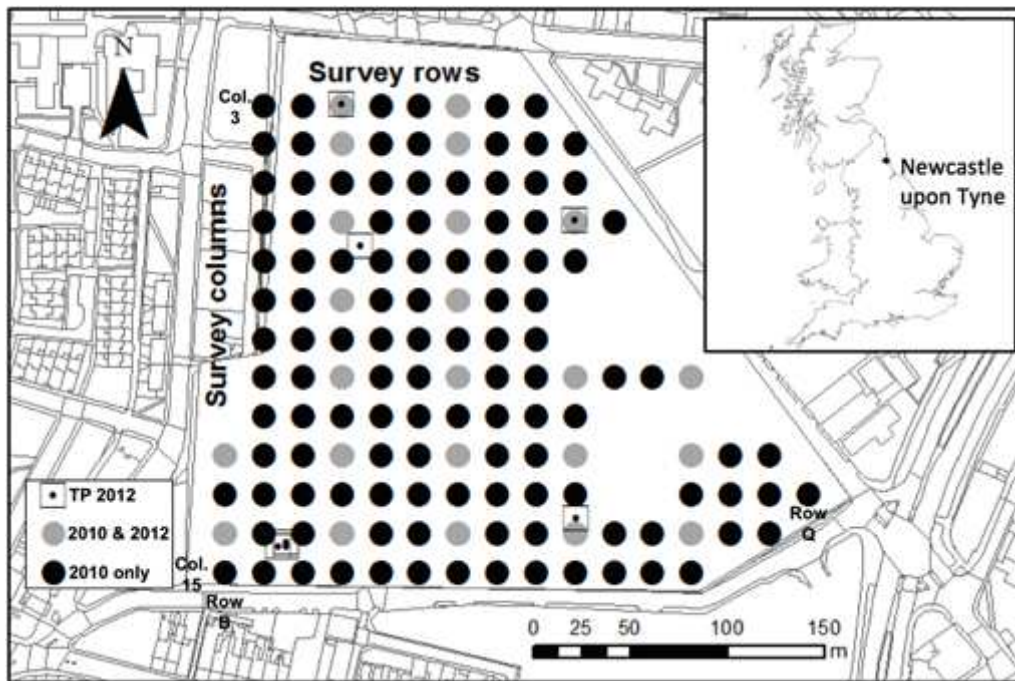


Figure 1. Location of study site, 2010¹⁷ (2010 spatial data points used in this figure are taken from Washbourne et al 2012) and 2012 sample points, and 2012 trial pit (TP) locations.

Methods used are described fully in Supporting Information (SI), with full details of analytical accuracy and precision. Bulk carbonate was determined for 95 samples (72 for 2010, 23 for 2012) using an Eijkelkamp calcimeter (BS 7755-3.10:1995)²³, and organic (not reported here) and inorganic carbon content determined using a Leco CS-244 Carbon / Sulfur Determinator. Stable isotope ratios of C and O were determined for 18 (9 for 2010, 9 for 2012) samples by Iso-Analytical, Cheshire UK, using a Europa Scientific 20-20 continuous-flow isotope ratio mass spectrometer (IRMS). Radiocarbon (¹⁴C) measurement was carried out on 2 samples (2010 sampling round) at the Scottish Universities Environmental Research Centre (SUERC) using an NEC Single Stage Accelerator Mass

Spectrometer.^{24,25} X-Ray Fluorescence (XRF) analysis was conducted on 14 samples (7 = 2010, 7 = 2012) at the University of Leicester Department of Geology using a PANalytical Axios Advanced XRF spectrometer. X-Ray Diffraction (XRD) analysis was carried out on 4 samples (2 = 2010, 2 = 2012) at Newcastle University School of Chemical Engineering and Advanced Materials using a PANalytical X'Pert Pro Multipurpose Diffractometer fitted with an X'Celerator detector and a secondary monochromator. Thermogravimetry-differential scanning calorimetry coupled with quadrupole mass spectrometry (TG-DSC-QMS) was conducted for 6 samples (3 = 2010, 3 = 2012) using a Netzsch Jupiter STA449C TG-DSC system connected to a Netzsch Aeolos 403C QMS.

Results and discussion

Surface soils (0-100 mm) were sampled systematically on two occasions 18 months apart, with very precise location (within 25 mm). All samples were analysed immediately following collection (SI, Table 1). Where analyses were carried out on smaller subsets of surface samples these were selected primarily to provide spatially even, distributed coverage across the study site.

The soil samples are similar in colour and particle size distribution to those reported previously¹⁷. Soil pH was consistently high (>9.5) with values up to 11.7¹⁷.

Two methods of determination, calcimeter and Leco analysis (total carbon – organic carbon), give closely corresponding soil CaCO₃ contents. Calcimeter analysis reported bulk equivalent CaCO₃ contents of 39.4 ± 8.1 wt% (range 26.5 - 61.4 wt%; 2010 samples analytical precision (standard error of the mean; SEM) ± 0.73 wt%; 2012 samples SEM = \pm

0.21 wt%). Leco analysis reported an average inorganic carbon content of 4.1 ± 1.2 wt% (range 3.0 - 7.1 wt%; SEM ± 0.48 wt%), corresponding to CaCO_3 concentrations of 38.9 ± 15.6 wt% (range 25.2 - 59.1 wt%; equivalent analytical precision ± 4.0 wt%).

Fig. 2A illustrates data from the depth to which trial pit samples could be taken during the sampling programme, however the total depth of material greatly exceeds this at some points across the site.¹⁷ Trial pit samples to approx. 1 m depth have CaCO_3 contents varying from 0.0 to 97.3 wt% CaCO_3 , with an average value of 19.1 wt% excluding a single outlier (97.3 wt% CaCO_3), which likely corresponds to inclusion of limestone aggregate (Fig. 2A; variability with depth is due to changes in ground conditions). The average carbonate content for trial pits from approx. 0 - 3 m depth, calculated from Leco total inorganic carbon data, is 15.9 ± 9.7 wt% CaCO_3 . CaCO_3 content does not vary with depth in a consistent manner across the site; nevertheless, the trial pit data generally show little variation with depth to 1.5m or greater. A number of the trial pits have anomalously high concentrations of CaCO_3 close to the surface (<1.0m), and two exhibit a decline in concentration deeper than 1.0m. These observations could indicate a carbonation front moving to greater depth with time. Reasons for the observed variability can be attributed to heterogeneity in material composition and properties, and to site-specific properties such as drainage patterns.

Thermogravimetry-differential scanning calorimetry coupled with quadrupole mass spectrometry (TG-DSC-QMS) and X-Ray diffraction (XRD) analysis (SI, Fig. 1 and 2) confirm the presence of calcite as the dominant calcium carbonate mineral, and demonstrate the presence of portlandite (Ca(OH)_2).

Between sampling dates, the surface soil samples show a consistent and statistically significant increase in CaCO_3 content (Fig. 2B). A Shapiro-Wilk test was conducted on the data, which found a non-normal distribution for 2010 and normal distribution for 2012. Given this discrepancy a non-parametric test was run (Wilcoxon Signed Rank Test which is used to assess whether the rank of population mean values differ between related samples) producing a significance value of 0.000, allowing the rejection of the null hypothesis (at 95% confidence) that the difference in the samples was due to chance. The starting composition of the material with respect to CaCO_3 is not known, but can be assumed to be small (but non-zero) due to possible inclusion of limestone aggregate or concrete carbonation occurring over the life of the now demolished structures. Overall, the CaCO_3 content to 100 mm depth over 18 months (2010-2012) increases from 22.0 wt% to 39.0 wt%. The range of the entire sample data is from 5.3 to 43.0 wt% CaCO_3 in 2010 and for the repeat samples 26.5 to 61.4 wt% CaCO_3 in 2012. Standard deviations are higher (8.3 wt%) in 2012 (6.9 wt% in 2010), which may reflect variable progress of the carbonation reaction occurring in a geochemically heterogeneous environment.

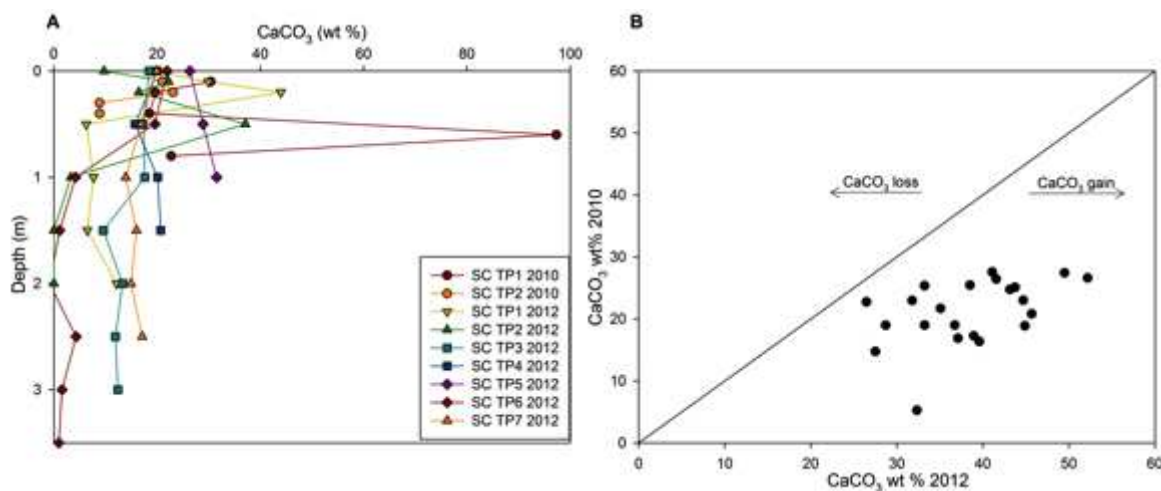


Figure 2. Calcium carbonate contents of urban soils determined by calcimeter analysis. A) variation in calcium carbonate content with depth from trial pit samples (N = 51) ; B) Increase in CaCO₃ concentration from 2010 to 2012 from surface samples; analytical error within size of symbol in both plots (comparative data 2010/12 N = 23).

A number of studies²⁶⁻²⁸ have illustrated that the stable isotope signatures of carbon and oxygen can be used to assess sequestration of CO₂ in recently formed pedogenic inorganic carbonates. Non-equilibrium stable isotope signatures are common in carbonate minerals formed from high pH brines. Thus, non-equilibrium isotope fractionation must be considered in studies of weathering and carbonation of portlandite, Ca(OH)₂, which releases hydroxyl ions into solution (hydroxylation), thereby increasing pH. Hydroxylation occurs at high pH (pH > 11.5)²⁶, in environments corresponding to those dominated by the weathering of artificial minerals in construction materials, as at Science Central. The C isotope signature is governed by diffusion of CO₂ into aqueous solution and subsequent precipitation of CaCO₃. The rate of hydroxylation exerts the greatest influence on the

isotope signature of high pH solutions and can be assigned a large role in determining the isotopic composition of carbonates formed from the weathering of artificial minerals in soil settings. Stable isotopic analysis of secondary carbonate minerals forming under ambient conditions that are relevant to soils confirms that a significant proportion of the carbonate carbon has been sequestered from the atmosphere in this way.²⁹

C and O isotope data for Science Central have $\delta^{18}\text{O}$ values between -10.0‰ and -13.8‰ and $\delta^{13}\text{C}$ values between -6.5‰ and -14.6‰ (all V-PDB; 2010 samples SE = $\pm 0.03\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.06\text{‰}$ for $\delta^{18}\text{O}$; 2012 samples SE = $\pm 0.04\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.03\text{‰}$ for $\delta^{18}\text{O}$). Between the two sampling dates, the mean $\delta^{13}\text{C}$ values change from -9.9 to -12.6‰, and $\delta^{18}\text{O}$ from -10.7 to -12.6‰. The shift towards more negative values is expected if the carbonate present includes a higher proportion produced following hydroxylation. The data shown in Fig. 3 represent mixtures of CaCO_3 derived from geological (lithogenic) sources (such as limestone aggregate in construction materials) and carbonate that originates through hydroxylation of CO_2 at high pH⁹, forming a linear plot representing mixing between lithogenic and pedogenic carbonates⁹. Similar arrays of data are reported for mortar²⁷ and carbonate precipitates from the underside of concrete structures.³³

A mixing line is superimposed on the data¹⁷, which assumes a lithogenic end member value for $\delta^{18}\text{O} = -0.0\text{‰}$, $\delta^{13}\text{C} = -0.0\text{‰}$, and a hydroxylation (high pH) end member $\delta^{18}\text{O} = -20.5\text{‰}$ (assuming meteoric water $\delta^{18}\text{O} = -7.8\text{‰}$ vs SMOW), $\delta^{13}\text{C} = -25.3\text{‰}$.^{9,17,26,28,30,31} (SI, Fig. 3). Other studies consider mixing between lithogenic carbonate and a ‘biogenic’ end member, with $\delta^{18}\text{O} = -6.8\text{‰}$ and $\delta^{13}\text{C} = -8.0\text{‰}$, attributed to photosynthesis.^{9,32} As the soils investigated in this study have little plant cover, and the observed range of $\delta^{18}\text{O}$ and

$\delta^{13}\text{C}$ extends to more negative values, it is assumed that photosynthetic inputs to newly formed soil carbonate are negligible. Thus on the basis of mixing between lithogenic and pedogenic carbonate formed at high pH, proportions of each component vary from 42 - 80% lithogenic and 58 - 20% hydroxylation (mean hydroxylation = 50%).

The data shown in Fig. 3 represent mixtures of CaCO_3 derived from geological (lithogenic) sources and carbonate that is assumed to have originated more recently through the hydroxylation of CO_2 at high pH.⁹ ^{14}C measurements (2 samples selected from the extremes of the observed range of the $\delta^{13}\text{C}$ data) suggest that a significant proportion of the C present in carbonates originates from the modern atmosphere (i.e. non-lithogenic sources). A value of $30.4 \pm 0.1\%$ Modern Carbon was found for a sample with $\delta^{13}\text{C} = -3.13\text{‰}$ (B15) and $80.7 \pm 0.4\%$ Modern Carbon for a sample with $\delta^{13}\text{C} = -13.55\text{‰}$ (J11; points are indicated in Figure 3) Full ^{14}C data in SI, Table. 2. This is consistent with increased incorporation of carbon from the modern atmosphere in samples that show most reaction.

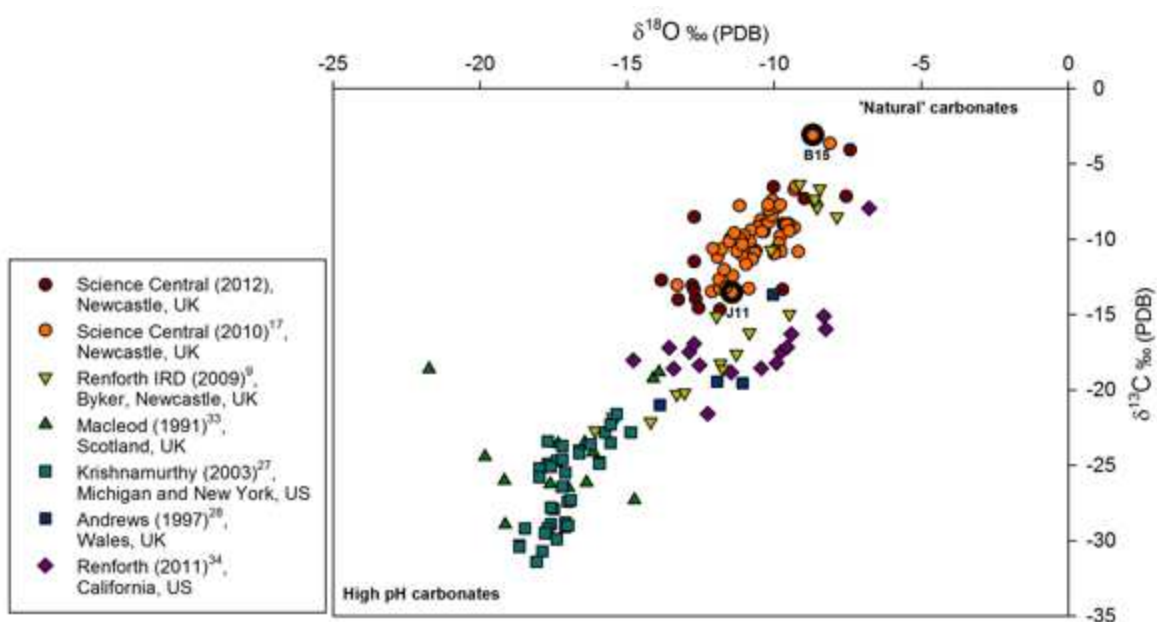


Figure 3. Stable isotopic data of samples from Science Central: $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ ‰ (V-PDB) (repeatability error bars are within point, in comparison with IRMS values from other sites (UK: 8, 26, 28; US: 25, 29)) (N = 185). ^{14}C sample points B15 and J11 indicated.

Variation in CaCO_3 content with depth depends on ground conditions, as noted in previous sections. In general, homogeneously crushed demolition material was found to depths of at least 1 m, extending deeper than this in some cases. Based on the observed change between 2010 and 2012 in CaCO_3 content of surface samples from 370 to 660 t ha^{-1} ($0.037 - 0.066 \text{ t m}^{-2}$), the rate of precipitation of calcium carbonate in the top 100 mm of soil is estimated to be 16 t ha^{-1} (0.0016 t m^{-2}) per month, or 192 t ha^{-1} (0.0192 t m^{-2}) annually. This corresponds to carbon removal from the atmosphere equivalent to 85 $\text{t CO}_2 \text{ ha}^{-1}$ ($0.0085 \text{ t CO}_2 \text{ m}^{-2}$) annually, or an annual increase in soil C content of 23 t C ha^{-1} ($0.0023 \text{ t C m}^{-2}$).

The measured soil inorganic carbon stock to 100 mm depth increased from 44 to 79 t C ha^{-1} ($0.0044 - 0.0079 \text{ t C m}^{-2}$) in 18 months, approaching values similar to those reported for organic carbon in arable land (84 t C ha^{-1} ($0.0085 \text{ t C m}^{-2}$)).³⁵ The rate of increase inferred from the observed change at Science Central exceeds estimates for soil carbon increases in rural land use (e.g. $3.63 \text{ t C ha}^{-1} \text{ a}^{-1}$ ($0.363 \text{ kg C m}^{-2} \text{ a}^{-1}$) through establishment (for example) of new woodlands).³⁶ It is likely that the observed rate will change with time, but it is not possible to measure changes at the site since 2012 due to more recent construction activity.

Soil carbon stocks are conventionally reported to greater depths than 100 mm.¹⁰ Figure 4 summarises CO_2 removal, extrapolating to 0.5 m depth on the basis of the consistent CaCO_3 contents to that depth from trial pit samples (see Fig. 2A) The extrapolation in

Figure 4 is based upon trial pit data to 0.5m and analytical data, assuming a contemporary mean CaCO_3 content of 20 ± 12.3 wt% (mean CaCO_3 content from trial pits to 0.5m and surface samples = 19.5wt %) and assuming that the proportion of carbonate newly formed (shortly prior to, or since demolition) through hydroxylation is 50% overall.



Figure 4. Observed carbon capture at Science Central, Newcastle (N = 23) (Contour map plotted using ArcGIS 10. Overlay created in Adobe Photoshop and Illustrator)

The calcium required for the carbonation reaction derives from two sources. First, dissolution of the cement mineral portlandite ($\text{Ca}(\text{OH})_2$) can provide readily-available Ca. The portlandite content of the samples was not quantified, but is typically around 15% in hydrated cement (~ 5% in concrete).³⁷ Secondly, dissolution of artificial Ca-bearing

silicates (amorphous or poorly crystalline phases; part of the cement clinker) occurs as cement weathers within the soil. An estimate of the rate of weathering of the silicate components of the soil has been made using the change in bulk composition determined by XRF (SI, Table 3), which shows a negative correlation between SiO_2 and CaO , consistent with the formation of calcite and proportionate reduction in the silicate minerals fraction. However, once normalised to TiO_2 (assuming Ti to be immobile during weathering)³⁸, the loss of SiO_2 exceeds that corresponding to dilution by newly-formed carbonate minerals. The observed loss of 20% of the SiO_2 content is equivalent to a weathering rate of $10^{-12.7}$ mol (Si) $\text{cm}^{-2} \text{s}^{-1}$ (normalised to a nominal mineral surface area of $1 \text{m}^2 \text{g}^{-1}$, conservatively estimated from particle size distribution¹⁷ and assuming 1 Mt of material onsite²²) or $16,000 \text{ t (Si) km}^{-2} \text{a}^{-1}$ (when normalised to the site area). It is assumed that Si is removed from the site in drainage waters, although some may have been retained in the formation of clay minerals (identified by XRD analysis). This is several orders of magnitude slower than dissolution rates for hydrated cement minerals determined through laboratory experiments ($10^{-8.0}$ mol (Ca) $\text{cm}^{-2} \text{s}^{-1}$)¹⁷, but is two orders of magnitude faster than the greatest weathering rates for natural catchments (e.g. a global average of $24 \text{ t km}^{-2} \text{a}^{-1}$,³³ or $100 \text{ t km}^{-2} \text{a}^{-1}$ for tropical volcanic arcs.⁴⁰ Enhanced SiO_2 removal is consistent with the high pH of this anthropogenic soil, and may explain the elevated weathering rate measured from rivers draining urbanised catchments.⁴¹

The significance of the results reported here is the demonstration of the very rapid and substantial rate of removal of CO_2 from the atmosphere by carbonation reactions that take place within soils that contain reactive calcium minerals. Similar observations have been found other sites, where the rate of CO_2 removal has been estimated based on the

285 assumption that calcium carbonate content in soil was zero at the time of demolition⁹ or soil
286 formation¹⁴. In urban soils, the dominant calcium silicate flux to soil is by incorporation of
287 demolition materials. Carbonation of artificial cement replaces CO₂ lost during
288 manufacture which involves calcining limestone (globally 5% of anthropogenic
289 emissions)⁴², thus closing one loop of the carbon cycle but not compensating for CO₂
290 produced by combustion of fuel used in the calcining process. Science Central represents a
291 single 10 ha site, but is typical of modern development practice that involves on-site
292 crushing of materials and the retention of crusher ‘fines’ on site as part of the soil. Urban
293 land in the UK represents 7% (or 1.7 million ha) of the country’s 25-million ha area⁴³. If
294 only 12,000 ha (or 0.7%) of urban soils in the UK were managed in a similar way to
295 Science Central, they could have the potential to remove 1 Mt CO₂ annually over the period
296 in which they are sequestering carbon dioxide, contributing to the requirement for the UK
297 carbon account for 2050 to be at least 80% lower than the 1990 baseline.⁴⁴

298 There are several considerations around the effective management of these sites to
299 maximise carbon capture, including the rate and thickness at which materials are emplaced,
300 how long the site remains undeveloped and the manner in which it might be covered by
301 buildings or by landscaped topsoil. Science Central is typical of redevelopment land, where
302 demolition materials are emplaced to variable depth (1 to 10’s of metres) on sites that may
303 remain undeveloped for 5 years or more. Carbonation appears to decrease with depth, likely
304 due to the isolation of materials from the atmosphere, therefore management which
305 increases atmospheric exposure (e.g. through appropriate planting that takes CO₂ to depth
306 via plant root systems and associated metabolism) is likely to increase carbonation rates

throughout the site.^{14,45,46} There is evidence that this carbon capture process occurs at other sites where topsoil has been emplaced.⁹ If the soil is covered by a building or impermeable pavements it will be isolated from the atmosphere, due to a ‘capping’ effect. By analogy with natural systems carbonate material formed whilst sites are undeveloped is likely to be stable and remain in the soils during and after redevelopment has taken place.⁴⁷

Globally, appropriate management of land as part of the development or reconstruction of sites where concrete structures have been demolished or destroyed should be considered as a way of partly compensating for emissions associated with the loss of CO₂ from firing carbonate raw materials (around 50% of the total CO₂ emissions of a kiln).⁴⁸ However, the cement industry will have to rapidly decarbonise in the coming decades to meet emission reduction targets (including wide-scale deployment of carbon capture and storage of kiln flue gasses). The post-use recarbonation of cement at the end of life of a structure, through soil processes, could result in a net negative carbon life cycle if combined with mitigation at the kiln. Approximately 3×10^9 t of cement is produced annually, emitting approximately 1.5×10^9 t CO₂ from chemical decarbonation.⁴⁹ Given the average building lifespan is around 50 years, this material could become available by mid century, representing a substantial carbon capture opportunity for the industry.

Although reported here for urban soils with artificial mineral inputs, calcite precipitation has also been observed in artificial soils prepared by blending natural calcium silicate rocks with compost.¹⁴ In the long term, a proportion of the calcite may dissolve, contributing to bicarbonate in groundwater and surface water (fluxes similar to those from outcropping natural carbonate-cemented sandstones). The potential for carbon capture as calcite

precipitated in soils with added calcium silicates has the potential to provide a passive carbon dioxide removal mechanism, analogous to the use of reed beds to clean contaminated surface waters.

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Supporting information available. This information is available free of charge via the Internet at <http://pubs.acs.org/>

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